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(54) Coloured hydrogel objects and their production.

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Description

The invention relates to colouring hydrogel objects to introduce colours desired for either protective masking or cosmetic purposes, and more particularly to colouring medical devices, such as ophthalmic contact lenses, for cosmetic or prosthetic reasons, or to protect the eyes from excessive light.

Several methods have been previously used to colour water-absorbent plastic articles using solvent, azoic and vat dyes, see, for example the following patents :

MESHEL
British Patent No. 1, 547, 525 (1979) ;
KOBERLEIN
United States Patent No. 2, 524, 811 (1950) ;
BRISTOL & SHERE
United States Patent No. 3, 519, 462 (1970) ;
WICHTERLE
United States Patent No. 3, 679, 504 (1972) ;
TANKA
United States Patent No. 4, 157, 892 (1979).

One of the main drawbacks of the processes of the above-mentioned patents, is that the colours produced are transparent. Consequently if an article such as a hydrogel contact lens is coloured in one of these ways, the effects obtainable are strictly limited. More particularly, if it is desired to change the colour of an eye, the colour obtained is the resultant of a combination of the natural colour of the eye and the colour of the contact lens. For example, a contact lens tinted with a transparent green colour will produce significantly different colour effects when placed on blue, green or grey eyes. Furthermore, it is not possible with such transparent coloured articles to produce any dramatic colour changes on people with dark eyes, such as brown or hazel eyes. Their use is consequently limited to light coloured eyes such as blue, green or grey eyes.

It has been proposed in United States Patent No. 3476499 (Wichterle) to precipitate an insoluble material in a hydrogel-type lens so as to absorb light. For example an impregnating agent is applied to one face of such a lens and a precipitating agent to the opposite face so that the two agents interact within the lens to form a solid water-insoluble precipitate. However it is disclosed that it is not always easy to obtain a precipitate of the desired density. For example if barium chloride solution is first applied to a hydrogel lens followed by sulphuric acid, most of the expected precipitate forms on the lens surface and can readily be removed by wiping.

United States Patent Specification 4634449 (Jenkins) describes a method for tinting a hydrogel contact lens in which a selected area of the lens is first rendered opaque, and the opaqued area is subsequently tinted. It is stated that a variety of opaquing materials can be used. More particularly, metallic silver, gold or platinum can be precipitated within the hydrogel by reduction of an appropriate salt or a silver halide can be precipitated in the hydrogel using silver nitrate and a halide salt. Advantage is taken of the fact that a silver halide can darken on exposure to light.

European Specification 122771A (Softint Inc.) describes soft contact lenses which are tinted by water-insoluble particles of that dye by a method in which pores of the hydrogel are impregnated with the leuco form of the dye and the insoluble vat dye is then precipitated in situ.

French Specification 2355642 (Toppan Printing Co. Ltd.) also describes a process for colouring a hydrogel resin, e.g. a contact lens, by impregnating the resin with a soluble colouring agent or a leuco derivative thereof and then rendering the colourant insoluble.

The present invention provides a method for colouring hydrogels and in particular for producing opaque or translucent colourations in a transparent hydrogel article. As compared with the process of USP 3476499, the new process is more reliable and more flexible. While the following description relates mainly to colouring hydrogel contact lenses, it will be understood that the method of the invention can in principle be used to colour any shaped article made of an organic polymer hydrogel. Using the new method it is possible to change the colour of any eye, whether brown, blue, hazel, green, grey or any other colour. This is achieved by introducing into a contact lens components which both provide the desired tint, and mask the colour of the natural eye, so that only the colour of the tint is effective. These components must be translucent or opaque to light in order to achieve this effect and must be capable of being formed in a hydrogel matrix and be capable, in the case of a hydrogel contact lens, of standing up to the cleaning or disinfecting regimes used in their care, and must not leach out of the lens matrix. They must also, of course, be physiologically innocuous. Preferably these components are not applied to the whole surface of the hydrogel, but only to selected areas, and especially an area corresponding to the iris of the eye, using suitable application, e.g. masking or printing, techniques.

The invention accordingly provides shaped organic polymer hydrogels containing within the gel an opaque or translucent, physiologically innocuous water-insoluble material which comprises a water-insoluble compound of barium or aluminium or zinc hydroxide in an amount sufficient to render at least part of the said hydrogel opaque or translucent, and a colouring agent for the hydrogel in at least part of the areas which have been rendered opaque or translucent by the said water-insoluble material. The opaque or translucent water-insoluble material may itself be slightly tinted, but the tint is mainly or completely provided by a separate material, and more particularly by

a disperse, solvent, vat, azo, or reactive dyestuff.

The invention also provides a method of making such a hydrogel which comprises applying to a shaped organic polymer hydrogel a solution of a water-soluble salt of barium, aluminium or zinc, in the presence if necessary of a swelling agent for said hydrogel so that the said solution penetrates substantially into the hydrogel, and then a reagent which reacts with the said salt to precipitate a water-insoluble compound of barium or aluminium or zinc hydroxide in situ in the hydrogel, and colouring at least part of the area in which the precipitate forms before, during, or after the formation of the said precipitate. It is important to ensure that the first solution substantially penetrates the hydrogel so that the precipitate is formed within, and not on, the hydrogel surface. With hydrogels containing large amounts of water, such penetration is automatic. With other hydrogels it is necessary to include in the first solution a swelling agent for the hydrogel which swells the hydrogel more than water to ensure that adequate penetration by the solution takes place. Suitable swelling agents include alcohols such as methanol or ethanol, acetone, ethylene glycol monomethylether and dimethylformamide.

The hydrogel material to which the invention is applied may be any known organic polymeric hydrogel of the kind out of which contact lenses are made, but is preferably a hydrogel as described and claimed in our British Specification No. 2087408. Such hydrogels combine a high water content and adequate mechanical properties with a low degree of cross-linking corresponding to less than 1% of cross-linking agent in many cases.

An aqueous solution of a water-soluble salt may be first applied to the hydrogel followed by a solution of a second reagent which reacts with the salt to produce a water-insoluble, opaque or translucent, physiologically innocuous precipitate. Suitable water-soluble salts are barium salts such as the chloride or nitrate, in which case the second reagent may be sulphuric acid or a water-soluble sulphate which reacts with the barium salt to produce white, highly water-insoluble barium sulphate.

The temperature at which the opaque precipitate is formed in the hydrogel is not critical and may be for example a temperature from ambient temperature up to 5°C lower than the boiling point of the reaction medium.

The treatment may be repeated if necessary to increase the opacity of the precipitate formed. Generally speaking the amount of water-insoluble material should be sufficient to mask the natural colour of the eye.

The invention is especially useful for making coloured contact lenses in which an area corresponding to the iris of the eye is coloured and areas corresponding to the pupil and the periphery of the lens are left transparent. Because the iris area is opaque, the new contact lenses are able to mask the natural colour of the eye and thus provide the possibility of lightening the eyes cosmetically. Similarly the new contact lenses may be used to mask eyes which are unnatural in appearance e.g. as a result of injury. In the latter case, the part overlaying the pupil should be dark coloured and preferably opaque.

The opaque or translucent material can be applied to the hydrogel before, after, or together with the colouring material, and the latter may be applied to the same areas as, or at least partly to areas different from, those covered by the opaque or translucent material.

A variety of inorganic materials can be used as the opaque or translucent component. In principle any water-insoluble compound of barium or aluminium or zinc hydroxide which is opaque to light, or substantially opaque, which is physiologically innocuous and which is not leached from the lens by the eye secretions, can be used. The preferred compounds are water-insoluble hydroxides, oxides, sulphates, or sulphides of aluminium or barium. The colour of the material must be compatible with the colour effect desired, and for this reason the preferred components are those which are white to yellow in colour. A preferred compound is barium sulphate, which can be precipitated as a white, non-toxic, water-insoluble solid in a hydrogel matrix by first soaking the matrix in an aqueous or aqueous/alcoholic (e.g. aqueous methanolic) barium chloride solution and then precipitating $BaSO_4$ by soaking the matrix in dilute sulphuric acid.

Suitable dyes which can be used to tint the hydrogels are Procion Turquoise SP-26, Procion Blue P-GR, Procion Brown P-GR, Procion Orange P-2R, CI Solubilized Vat Orange 5, CI Solubilized Vat Blue 6, CI Solubilized Vat Green 1, CI Solubilized Vat Brown 1, CI Dispersol Violet 28, Savinyl Blue GLS, Savinyl Green 2GLS, and Waxoline Red GPFW. For a natural effect the colouring agent should be applied in such a way that the intensity of colour is essentially constant over the whole of the coloured area apart from any deliberate patterning that may be introduced.

If desired patterns may be incorporated into the opaque material and/or the colouring agent, in order better to simulate the natural appearance of the eye. For example, by using standard printing (especially screen, pad or ink-jet printing) techniques, the opaque material may be formed in a pattern in the hydrogel. Such a pattern may be of continuous, straight, curved or zig-zag lines or of solid shapes such as triangles, parabolas, ellipses, or rectangles. The colouring may take place before or after such a printing operation. Similarly the colouring agent may be deposited as a pattern in a similar way and using similar techniques. Moreover, more than one colouring agent can be used.

For example a contact lens coloured in accord-

ance with the invention may be further coloured by applying a different transparent dyestuff to deposit a pattern over the iris section. To resemble the natural iris pattern, this second dyestuff is preferably a dark shade, e.g. black, grey, navy blue or brown. It may be applied by standard printing techniques. This pattern may be solid, continuous or intermittent, and should preferably cover at least 5 percent of the tinted area. By using this technique, the colour of the contact lens in use will be the resultant of the transparent tint enhanced with the pattern of the second transparent colour. Moreover if the opaque backing is patterned, it adds to the combined effect.

The invention is illustrated by the following Examples :

Example 1

A saturated aqueous solution of barium chloride was applied to a hydrogel contact lens, based on a copolymer of N-vinyl-pyrrolidone and a hydrophobic methacrylate, as described in British Patent 2087408, having a water content of 77%, for 10 minutes. The central 4 mm pupillary area and 2 mm of the outer peripheral area of the lens were masked. The lens was then treated with 2% H_2SO_4 solution for 2 minutes. An opaque pattern consisting of a white precipitate of barium sulphate was formed in the lens, the pupillary and peripheral areas of the lens being left clear.

The lens obtained was coloured with a solution of a reactive dye (Procion Green P-4BL) in water for 2 minutes, the pupillary and peripheral areas being masked.

A green opaque lens was obtained which had clear pupillary and peripheral areas. This lens was placed on a brown eye and was effective in masking the brown colour and turning the eye to green.

Similar results are obtained if the lens is tinted with other reactive, solubilised vat colours, solvent or disperse dyestuffs dissolved in water or a solvent such as acetone. The different coloured lenses obtained were effective in changing the colour of brown eyes.

Example 2

Example 1 was repeated using a saturated barium chloride solution in aqueous 30% or 50% methanol instead of water. A more dense opaque precipitate was obtained, than in Example 1 indicating a deeper penetration of the barium sulphate into the lens matrix, caused by the additional swelling of the hydrogel by the methanol. The opaque lens obtained (after tinting as described in Example 1) was placed on a brown eye and was effective in masking the brown colour.

The same result is obtained if the lens is first tinted and then treated as described in Example 2.

Example 3

An opaque white precipitate was obtained in a 2-hydroxy-ethyl methacrylate hydrogel, having a water content of 38%, using the method described in Example 2. This hydrogel was tinted as described in Example 1 to produce a coloured lens in accordance with the invention.

Example 4

Example 2 was repeated using aqueous Aluminium Sulphate or Zinc Chloride solution, followed by Sodium hydroxide solution, to form an opaque precipitate of insoluble Aluminium or Zinc hydroxide in the hydrogel. A mixture of barium sulphate and aluminium hydroxide was also precipitated in the lens using a two stage process.

All the lenses described in the above Examples were capable of effectively masking the colour of blue, green, grey or hazel eyes as well as brown eyes.

All the dyestuffs disclosed in the above Examples were applied to the hydrogel by standard techniques employed in the dyeing or printing industry, viz. dissolving the colourant in water and/or a solvent which is capable of swelling the hydrogel, applying the dye solution to selected areas of the hydrogel for a fixed time, followed by evaporating the solvent, or fixing or oxidizing the colourant to render it, in the hydrogel matrix, insoluble in water.

Example 5

The iris section of an opaque coloured contact lens produced in accordance with any of the Examples 1 to 4 was overprinted with a pattern of radiating straight lines by a screen printing process. This was achieved by dissolving 5% solubilised vat Brown dyestuff in hot water with 2% corn starch, and allowing the mixture to cool at room temperature to a paste which could be screen printed onto the hydrogel lens using a doctor blade. The screen was removed, and the lens allowed to stand for 10 minutes and then oxidised in a solution of 2% sulphuric acid containing sodium nitrite to regenerate the parent vat dye. An opaque coloured lens with patterned brown lines was obtained.

This Example was repeated using other viscosity enhancing agents, e.g. cellulose derivatives, alginates, gums, glycerol, other starches instead of corn starch, in a quantity to prevent the colour spreading or smudging after removing the screen, to produce patterns on the lens.

Pad printing or ink jet printing may be used in place of screen printing.

Example 6

Example 5 was repeated using other classes of dyestuffs such as reactive, solvent, or disperse dyestuffs using the appropriate solvent to dissolve the dyestuff and a compatible viscosity enhancing agent to obtain similar patterns on the lenses.

Example 7

Example 5 was repeated using other patterns such as curved or zig-zag or intermittent broken lines or solid shapes such as triangles, parabolas, ellipses, circles or rectangles or combinations of the above to obtain a variety of patterned lenses.

Example 8

The opaque coloured patterns can also be formed by screen printing, pad printing, or ink jet printing techniques using suitable viscosity enhancing agents as described in Example 5, e.g. as follows.

A paste containing 2% corn starch and 10% barium chloride was made up in hot water and allowed to cool to room temperature. This paste was printed as a pattern consisting of straight parallel radiant lines, on the iris section of a contact lens containing 67% water by a screen printing process. The lens was allowed to stand for 2 minutes and then developed in a 2% sulphuric acid solution to precipitate insoluble barium sulphate in the lens matrix in the form of the applied pattern. These lenses were then tinted with a solvent, reactive, disperse or vat dye as described in the foregoing Examples to give a patterned lens which, when placed on a dark brown eye, was effective in changing the colour of the eye and looked natural.

Pad printing or ink jet printing may be used in place of screen printing.

Other patterns as described in Example 7 can also be obtained. The patterns produced can be made of continuous lines or shapes rather than dotted lines or shapes.

Claims

1. A shaped organic polymer hydrogel containing within the gel an opaque or translucent, physiologically innocuous, water-insoluble material which comprises a water-insoluble compound of barium or aluminium or zinc hydroxide in an amount sufficient to render at least part of said hydrogel opaque or translucent, and a colouring agent for the hydrogel in at least part of those areas containing the said water-insoluble material.

2. A shaped hydrogel according to claim 1 in the form of a contact lens in which the part overlaying the iris of the eye is coloured and opaque and the part overlaying the pupil of the eye is transparent.

3. A shaped hydrogel according to claim 2 in which the said part overlaying the iris of the eye has an opaque, white to yellow, and optionally patterned backing and one or more transparent colouring agents deposited uniformly or in a pattern over at least part of the said backing.

4. A shaped hydrogel according to claim 1 for cosmetic or prosthetic purposes in the form of a contact lens in which the part overlaying the iris of the eye is coloured and opaque and the part overlaying the pupil of the eye is dark coloured.

5. A shaped hydrogel according to claims 1 to 4 which contains a dye as the said colouring agent.

6. Method of making a shaped hydrogel as claimed in claim 1 which comprises applying to a shaped organic polymer hydrogel a solution of a water-soluble salt of barium, aluminium or zinc in the presence, if necessary, of a swelling agent for said hydrogel so that the said solution penetrates substantially into the hydrogel, and then a reagent which reacts with the said salt to precipitate a water-insoluble compound of barium or aluminium or zinc hydroxide in situ in the hydrogel, and colouring at least part of the area in which the precipitate is formed before, during or after the formation of the said precipitate.

7. Method according to claim 6 in which the said swelling agent is methanol, ethanol, acetone, ethylene glycol monomethyl ether, or dimethylformamide.

8. Method according to claim 6 or 7 in which the water-insoluble precipitate is barium sulphate, aluminium hydroxide, or zinc hydroxide or a mixture thereof.

9. Method according to any of claims 6 to 8 in which the solution of the water-soluble salt is applied uniformly or in a pattern to the hydrogel by screen printing, pad printing, or ink jet printing.

10. Method according to any of claims 6 to 9 in which a solvent, disperse, vat, or reactive dyestuff is used to colour the hydrogel in at least part of the areas containing the said water-insoluble compound or zinc hydroxide before, during or after the said material is precipitated in the said hydrogel.

11. Method according to claim 10 in which the dyestuff is applied uniformly or in a pattern by screen printing, pad printing or ink jet printing.

Ansprüche

1. Geformtes organisches Polymer-Hydrogel, enthaltend innerhalb des Gels ein opakes oder durchscheinendes, physiologisch unschädliches, wasserunlösliches Material, anfassend eine wasserunlösliche Verbindung von Barium oder Alumi-

nium oder Zinkhydroxid in einer Menge, die ausreicht, mindestens einen Teil des Hydrogels opak oder durchscheinend zu machen, und ein Färbemittel für das Hydrogel in mindestens einem Teil derjenigen Bereiche, die das wasserunlösliche Material enthalten.

2. Geformtes Hydrogel nach Anspruch 1 in Form einer Kontaktlinse, in der der Teil, der auf der Iris des Auges aufliegt, gefärbt und opak ist und der Teil, der auf der Pupille des Auges aufliegt, transparent ist.

3. Geformtes Hydrogel nach Anspruch 2, wobei der Teil, der auf der Iris des Auges aufliegt, einen opaken, weiß bis gelben und gegebenenfalls gemusterten Hintergrund aufweist und wobei ein oder mehrere transparente Färbemittel gleichmäßig oder in einem Muster auf mindestens einem Teil des Hintergrundes abgeschieden sind.

4. Geformtes Hydrogel nach Anspruch 1 für kosmetische oder prothetische Zwecke in Form einer Kontaktlinse, bei der der Teil, der auf der Iris des Auges aufliegt, gefärbt und opak ist und der Teil, der auf der Pupille des Auges aufliegt, dunkel gefärbt ist.

5. Geformtes Hydrogel nach Ansprüchen 1 bis 4, das einen Farbstoff als Färbemittel enthält.

6. Verfahren zur Herstellung eines geformten Hydrogels nach Anspruch 1, umfassend das Aufbringen einer Lösung eines wasserlöslichen Salzes von Barium, Aluminium oder Zink auf ein geformtes organisches Polymer-Hydrogel in Gegenwart, soweit erforderlich, eines Quellmittels für das Hydrogel, so daß die Lösung im wesentlichen in das Hydrogel eindringt, und anschließend eines Reagens, das mit dem erwähnten Salz reagiert, an eine wasserunlösliche Verbindung von Barium oder Aluminium oder Zinkhydroxid in situ in dem Hydrogel auszufällen, und Färben mindestens eines Teils des Bereichs, in dem der Niederschlag entstanden ist, vor, während oder nach der Bildung des erwähnten Niederschlags.

7. Verfahren nach Anspruch 6, wobei das Quellmittel Methanol, Ethanol, Aceton, Ethylenglykolmonomethylether oder Dimethyl-formamid ist.

8. Verfahren nach Anspruch 6 oder 7, wobei der wasserunlösliche Niederschlag Bariansulfat, Aluminiumhydroxid oder Zinkhydroxid oder ein Gemisch davon ist.

9. Verfahren nach einem der Ansprüche 6 bis 8, wobei die Lösung des wasserlöslichen Salzes gleichmäßig oder in einem Muster auf das Hydrogel durch Siebdruck, Klotzen oder Spritzdüsendruck aufgebracht wird.

10. Verfahren nach einem der Ansprüche 6 bis 9, wobei ein Lösungsmittel-, Dispers-, Küpen- oder Reaktivfarbstoff angewandt wird, an das Hydrogel in mindestens einem Teil der Bereiche zu färben, die die erwähnte wasserunlösliche Verbindung oder Zinkhydroxid enthalten, vor, während oder nachdem das Material in dem Hydrogel ausgefällt worden ist.

11. Verfahren nach Anspruch 10, wobei der Farbstoff gleichmäßig oder in einem Muster durch Siebdruck, Klotzen oder Spritzdüsendruck aufgebracht wird.

Revendications

1. Un hydrogel polymère organique façonné contenant à l'intérieur du gel une matière opaque ou translucide, physiologiquement inoffensive, insoluble dans l'eau qui comprend un composé insoluble dans l'eau du baryum ou de l'aluminium ou l'hydroxyde de zinc en quantité suffisante pour rendre au moins une partie dudit hydrogel opaque ou translucide, et un agent colorant pour l'hydrogel dans au moins une partie des zones contenant ladite matière insoluble dans l'eau.

2. Un hydrogel façonné selon la revendication 1, sous la forme d'une lentille de contact dans laquelle la partie qui recouvre l'iris de l'oeil est colorée et opaque et la partie qui recouvre la pupille de l'oeil est transparente.

3. Un hydrogel façonné selon la revendication 2, selon laquelle ladite partie qui recouvre l'iris de l'oeil a une couche de renforcement opaque, du blanc au jaune, et portant éventuellement un motif et un ou plusieurs agents colorants transparents déposés uniformément ou selon un motif sur au moins une partie de ladite couche de renforcement.

4. Un hydrogel façonné selon la revendication 1, pour des applications cosmétiques ou prosthétiques sous la forme d'une lentille de contact dans laquelle la partie qui recouvre l'iris de l'oeil est colorée et opaque et la partie qui recouvre la pupille de l'oeil est de couleur foncée.

5. Un hydrogel façonné selon les revendications 1 à 4, qui contient un colorant en tant que ledit agent colorant.

6. Méthode de préparation d'un hydrogel façonné selon la revendication 1, qui consiste à appliquer à un hydrogel polymère organique façonné une solution d'un sel soluble dans l'eau de baryum, d'aluminium ou de zinc en présence, si nécessaire, d'un agent de gonflement pour ledit hydrogel de sorte que ladite solution pénètre substantiellement dans l'hydrogel, et ensuite un réactif qui réagit avec ledit sel pour précipiter un composé insoluble dans l'eau du baryum ou de l'aluminium ou l'hydroxyde de zinc in situ dans l'hydrogel, et à colorer au moins une partie de la zone dans laquelle le précipité est formé avant, durant, ou après la formation dudit précipité.

7. Méthode selon la revendication 6, selon laquelle ledit agent de gonflement est le méthanol, l'éthanol, l'acétone, l'éther monométhylique de l'éthylèneglycol ou le diméthylformamide.

8. Méthode selon la revendication 6 ou 7, selon laquelle le précipité insoluble dans l'eau est le sulfate de baryum, l'hydroxyde d'aluminium ou l'hydroxyde

de zinc ou un mélange de ceux-ci.

9. Méthode selon l'une quelconque des revendications 6 à 8, selon laquelle la solution du sel soluble dans l'eau est appliquée uniformément ou selon un motif à l'hydrogel par impression au pochoir, par impression par foulardage, ou par impression au jet d'encre.

10. Méthode selon l'une quelconque des revendications 6 à 9, selon laquelle un colorant à solvant, un colorant de dispersion, un colorant de cuve, ou un colorant réactif est utilisé pour colorer l'hydrogel dans au moins une partie des zones contenant ledit composé insoluble dans l'eau ou l'hydroxyde de zinc avant, pendant, ou après la précipitation de ladite matière dans ledit hydrogel.

11. Méthode selon la revendication 10, selon laquelle le colorant est appliqué uniformément au selon un motif par impression au pochoir, impression par foulardage ou impression par jet d'encre.